Potassium permanganate

CAS ID: 7722-64-7

Chemical formula: $KMnO_4$

Synonyms / Trade names: Permanganate of potash, Cairox®, Chameleon mineral, Condy's crystals

Chemical composition: Potassium permanganate is a crystalline inorganic solid which decomposes (it does not actually melt) at 240° C. In its solid form, the crystals appear as a shiny, dark purple to black solid. Its solubility in water is approximately 64,000 mg/L. Concentrated aqueous solutions appear purple in color, while more dilute solutions appear light purple or pink. Its molecular weight is 158.034. Manganese within potassium permanganate is in its +7 valence state, which results in $KMnO_4$ being a strong oxidizing agent due to the reduction of the heptavalent manganese. Potassium permanganate solutions used at fish hatcheries contain between 1 - 10 mg/L $KMnO_4$ in water bath or flow through exposures, with an exposure duration of up to one hour (AFS 2011).

Hatchery use: Potassium permanganate is normally administered in a static bath to control external protozoan and metazoan parasites, and bacterial and fungal infections. Based on the permanganate demand of hatchery water, exposure concentrations range between 2 – 10 mg/L, applied in 2 mg/L increments until an effective concentration is found for the specific hatchery (Francis-Floyd and Klinger 2002). Exposure durations at hatcheries range between 30 – 60 minutes/day. Although fish are normally exposed to only a single $KMnO_4$ exposure, treatments can be safely repeated on multiple days. Potassium permanganate is currently in a deferred regulatory status according to the FDA, meaning that it not a low regulatory priority chemical, however the FDA has deferred regulatory action pending further study. EPA has registered potassium permanganate for use in fish hatcheries as a pesticide. No Washington hatcheries discharging to estuarine or marine waters report using potassium permanganate. Thus, if current use patterns continue, potassium permanganate should have no effect on any estuarine or marine T&E fish species. The only hatchery in Washington currently reporting use of potassium permanganate is the Keta Creek Fish Hatchery, which discharges to freshwater systems. Keta Creek hatchery reports using $KMnO_4$ at an exposure concentration of 2 mg/L.

Measures of Exposure:

The use of potassium permanganate in hatcheries is generally for the control of external protozoan, metazoan, bacterial and fungal infestations. Application is generally at a concentration between 1 – 10 mg/L to fish. The Keta Creek hatchery reports using $KMnO_4$ at a concentration of 2 mg/L, however, they do not report the exposure duration of fish to $KMnO_4$, the number of days/year $KMnO_4$ treatments are employed, or the volume of the tanks in which fish are exposed to $KMnO_4$.

The lack of detailed use information for potassium permanganate from Keta Creek hatchery required EPA to make several assumptions regarding their KMnO4 use, which directly impact the estimated environmental concentration calculations. These assumptions are presented in the Expected Environmental Concentration (EEC) portion of this Measures of Exposure section.

The remainder of this measures of exposure assessment will evaluate two aspects that combined define the exposure of ESA listed species to potassium permanganate in the environment: its environmental fate once released into the environment, and its expected environmental concentration.

Environmental Fate of Potassium Permanganate

This section will describe the expected environmental fate of potassium permanganate.

Chemically, potassium permanganate is a strong oxidant. Permanganate is not desirable when added to hatchery water in stoichiometric excess, for several reasons. Excess permanganate left over after it has completed disinfection and oxidation of organic matter present in water is stable, and can remain in solution for months in the absence of contact with any additional organic matter. This stoichiometric excess has the potential over time to both continue oxidizing naturally occurring organic matter in hatchery water, and to elicit long term toxicity to fish. Excess permanganate also imparts an undesirable pink or purple color to water.

Oxidizing agents such as $KMnO_4$ release one or more reactive oxygen species (ROS), which are a group of free radical chemical species capable of existing while containing one or more unpaired electrons. The unpaired electron(s) alters the chemical reactivity of the molecule or atom, making it more reactive than the corresponding non-free radical form. The oxygen free radicals include superoxide anion free radical ($\cdot O_2^-$), peroxide free radical ($\cdot O_2^{-2}$), hydroxyl free radical ($\cdot OH$) and perhydroxyl free radical ($\cdot HO_2$). Of these, the hydroxyl free radical is the most reactive, and thus capable of causing the greatest damage to external surfaces of cells and viruses. Singlet oxygen ($^1O_2$) is not, strictly speaking, a free radical, but it is an electrically excited state of molecular oxygen (O_2) that can also form during permanganate reduction, and is capable of irreversibly damaging cell membranes.

Free radicals and singlet oxygen irreversibly alter most biological macromolecules, including the proteins and lipids which constitute cell walls, cell membranes and viral envelopes. This irreversible alteration of the structure and function of biological macromolecules is responsible for the disinfecting properties of potassium permanganate, and is also why $KMnO_4$ acts as an external toxicant, not requiring uptake into the organism before eliciting toxicity.

Potassium permanganate undergoes violent combustion reactions with several classes of organic compounds, including alcohols, glycols and aldehydes (including formalin, which contains both formaldehyde and methanol).

The primary reactions of potassium permanganate in surface water include the following:

$$KMnO_4 + 2H_2O \leftrightarrow MnO_2 + KOH + 3OH^- \ (occurs\ between\ pH\ 3.5\ to\ 12)$$

$$2KMnO_4 \leftrightarrow K_2MnO_4 + MnO_2 + O_2 \ (photodecomposition)$$

$$2KMnO_4 + 2H_2O \leftrightarrow K_2MnO_4 + 2H^+ + \cdot OH \ (hydroxyl\ free\ radical\ production)$$

$$R + \cdot OH \leftrightarrow ROH \;\; (oxidation\ of\ organic\ matter\ (R)\ by\ hydroxyl\ free\ radicals)$$

A common reaction product of $KMnO_4$ is manganese dioxide (MnO_2), where manganese has been reduced from the +7 valence in $KMnO_4$ to the +4 valence in MnO_2. MnO_2 is a solid, common naturally occurring mineral, generally considered to be nontoxic, which in solution imparts a brown color to water. The above photodecomposition reaction, which forms potassium manganate (K_2MnO_4), MnO_2 and oxygen is the basis for the historical use of adding permanganate to water to increase its oxygen content.

Potassium permanganate has the ability to produce both hydroxyl ions (OH^-) and hydroxyl free radicals ($\cdot OH$) in surface water. Most organic matter, including cell membranes and viral envelopes, is quickly oxidized by the hydroxyl free radicals released during the transformation of potassium permanganate in surface water. This oxidation of organic matter with hydroxyl free radicals is the primary mechanism of toxic action by which $KMnO_4$ serves as a disinfectant.

Although aqueous potassium permanganate solutions are stable in the absence of light and organic matter, they are very reactive when organic matter is present. In the literature, reaction rates and half lives of permanganate reactions with organics are usually expressed in terms of concentrations of the organic compounds being reduced, not the concentration of $KMnO_4$ *per se*. But assuming stoichiometrically equivalent concentrations of organic matter and $KMnO_4$, the half-life of organic matter should be equivalent to the half-life of potassium permanganate.

Marking and Bills (1975) in their study of $KMnO_4$ toxicity to several fish species, also measured the ability of $KMnO_4$ to inactivate the piscicide antimycin. The half-life of the reaction using 1 mg/L $KMnO_4$ ranged between 7 – 11 minutes, depending on the pH of the water. Potassium permanganate oxidized a series of six chlorophenol compounds with half-lives ranging between 0.41 – 8.25 minutes (Hossain and McLaughlan 2013). With the exception of perchloroethylene (PCE), Huang et al. (2001) observed that potassium permanganate was able to oxidize a series of chlorinated ethylene compounds in half-lives of between 0.13 – 13.5 minutes. PCE was oxidized by permanganate with a half-life between 145 – 350 minutes (Huang et al. 2001). Naturally occurring humic acids in river water are readily oxidized by potassium permanganate (Xia et al. 2005). For many organic compounds in water, the half-life of potassium permanganate used to oxidize the organics would appear to be on the order of minutes. These short half-lives would appear to indicate that any potassium permanganate used in stoichiometric excess of hatchery needs would be quickly reduced to non-oxidizing compounds of low toxicity if released to the environment.

The long term stability of potassium permanganate in aqueous solutions in the absence of organic matter and light leads to a potential for some level of manganese bioaccumulation in aquatic species. This stability is unusual among the chemical oxidants and disinfectants used at hatcheries. Of the hatchery chemicals evaluated in this BE, potassium permanganate is the only one whose chemical structure includes a transition element metal potentially available to be bioaccumulated by aquatic species. A U.S. Fish and Wildlife Service white paper on potassium permanganate use in aquaculture (MacMillan 2009) identified studies where manganese uptake by fish was evaluated during exposure to $KMnO_4$. Studies with both channel catfish and rainbow trout observed no difference in manganese tissue concentrations between Mn-exposed and Mn-unexposed fish.

Expected Environmental Concentration (EEC) of Potassium Permanganate

The desired treatment concentration of potassium permanganate at the Keta Creek hatchery is 2 mg/L. Keta Creek also has provided EPA with their annual range of daily water discharges from the hatchery to receiving waters. Unfortunately, Keta Creek hatchery has been unable to provide EPA with information regarding the volume of potassium permanganate used per day or the number of days per year $KMnO_4$ is used. The volume of chemical used per day by a hatchery is an essential component of the calculation required to derive the expected environmental concentration (EEC) of potassium permanganate in water at the point where the hatchery discharges into a receiving water (i.e. the end of pipe $KMnO_4$ concentration). This end of pipe concentration is used as a conservative estimate of the potassium permanganate concentration in receiving waters prior to any dilution of hatchery discharges by the receiving body of water.

However, information about the size of raceways at Keta Creek can be used to estimate the volume of water in a raceway treated with potassium permanganate. According to Moore (2003), raceways at Keta Creek used to rear Chinook fry are 10’ x 100’ x 4’ in size. If completely full of water, a raceway would contain 4000 ft^3 of water, equivalent to 29,922 gallons. If it is assumed that a 2 mg/L concentration of $KMnO_4$ is maintained for the recommended one hour exposure (AFS 2011) in a volume of 29,922 gallons of water, and only one raceway at a time is treated, an estimate of the expected environmental concentration can be calculated.

As described in the Problem Formulation section of the methodology used in this BE, the EEC is calculated as follows, based on procedures described in Schmidt et al. (2007).

$$EEC = \frac{C \times V}{F + E}$$

Where: EEC = Expected environmental concentration (mg/L or µg/L)

C = Treatment concentration of chemical in the hatchery (mg/L or µg/L)

V = Volume of chemical used (gallons/day)

F = Volume of water discharged from hatchery to receiving water (gallons/day)

E = Effluent pond volume (gallons)

For the purposes of calculating the potassium permanganate EEC, EPA has assumed that the effluent pond volume is zero. The Keta Creek hatchery potassium permanganate concentration, estimated use volume, and the hatchery low, average and maximum daily discharges to receiving water are presented in Table PP-???, along with the calculated EEC for each of the three hatchery discharge volumes.

Table PP-???. Expected environmental concentration of potassium permanganate under low, average and high water volume daily discharges from the Keta Creek Fish Hatchery.

Parameter	Value	EEC (µg/L)
Chemical use concentration, mg/L	2	
Daily volume used, gallons	29,922	
Total volume used/year, gallons	Unknown	
Days/year chemical used	Unknown	
Low hatchery discharge, gallons/day	3,284,640	18.2
Average hatchery discharge, gallons/day	5,890,140	10.2
High hatchery discharge, gallons/day	10,540,300	5.7

The EEC concentrations from Table PP-??? will be compared to the chronic NOEC estimates calculated in the Measures of Effect section. This comparison will take place in the Risk Characterization section to estimate ecological risks to T&E species exposed to potassium permanganate discharges from hatcheries in Washington.

Measures of Effect:

For fully aquatic species, the available toxicity data was identified from a search in EPA's ECOTOX database (http://cfpub.epa.gov/ecotox/).

A combined total of 278 freshwater toxicity records were identified from the above search. These results are presented in Appendix ???, Table ??? As no Washington hatcheries discharging to marine or estuarine systems currently use potassium permanganate, no search was made for toxicity data to marine species. Of the freshwater records, only 12 report results for animals exposed to potassium permanganate under flow through conditions: 1 record for bluegill, 2 records for channel catfish, 3 records for the Asiatic clam *Corbicula manilensis*, and 6 records for the zebra mussel. The bluegill study and one of the *Corbicula manilensis* studies are of suitable quality for use in deriving water quality criteria. The zebra mussel studies are of chronic duration (up to 52 days exposure), but were focused on controlling, eliminating or preventing recolonization of zebra mussel accretions on intake pipes for potable water treatment systems. As such, the zebra mussel studies can be considered to represent lethal concentrations under chronic, long term exposures.

The remaining available toxicity data for aquatic species was performed under static, static renewal or pulsed exposures. Taxa for which potassium permanganate toxicity data are available that does not meet EPA requirements for use in deriving water quality criteria are as follows:

- Freshwater algae: 4 species
- Freshwater macrophytes: None
- Aquatic insects: 1 species
- Freshwater crustaceans: 11 species
- Freshwater zooplankton: 6 species
- Freshwater molluscs: 3 species
- Other freshwater invertebrate taxa (e.g. oligochaetes): 8 species
- Amphibians: None
- Freshwater fish: 21 species

As noted in the previous paragraph, the potassium permanganate toxicity to zebra mussel studies were focused on the use of controlling or eliminating their accretion on pipes or other structures. This type of study with $KMnO_4$ has not been limited to zebra mussels. Most of the potassium permanganate toxicity information on species other than fish has been limited to evaluation of its use as a biocide, where often the only reported endpoint is either a concentration or exposure duration required to elicit 100% mortality of the test species. Fish toxicity studies with potassium permanganate have been limited to evaluating its effects from exposure to its therapeutic dose. The fish studies have either extended the exposure of fish to the therapeutic dose from one hour to 96 hours (the standard test duration for acute lethality studies), or have exposed the fish either to the therapeutic dose or some multiple of the therapeutic dose for one hour, then placed the fish in clean water and monitored any residual toxicity that occurs once the fish is removed from the $KMnO_4$ solution. None of these types of toxicity studies readily lend themselves to evaluation of potassium permanganate toxicity to T&E species or their prey using the methodologies presented in the Problem Formulation section of this BE. This is because the tests are performed using non-standard test methodologies, report non-standard test endpoints, or both.

Some information is available indicating that the difference in lethal concentrations of $KMnO_4$ and no effect concentrations of $KMnO_4$ is small. This situation generally occurs for chemicals with steep dose-response curves, meaning the difference between adverse and no adverse effect concentrations for a given species may be small. Steep dose-response curves for chemicals acting as oxidants have been empirically identified for fish species (Tsai et al. 1990).

Of the available potassium permanganate toxicity studies, the single study that demonstrates the range of concentrations between lethal and no effect for the same species is that of Hobbs et al. (2006). Hobbs et al. (2006) measured 96 hour LC_{50} values of potassium permanganate for five species: *Daphnia magna*, *Ceriodaphnia dubia*, fathead minnow (*Pimephales promelas*), *Chironomus dilutus* and *Hyalella azteca*. *Daphnia* and *Ceriodaphnia*, as will be discussed in the toxicity to prey species of T&E species, are both crustacean zooplankton species, the group of species that appears to be more sensitive to potassium permanganate than any other taxonomic grouping of animals. Unlike nearly all other available $KMnO_4$ toxicity studies, the static renewal *Daphnia*, *Ceriodaphnia* and fathead minnow exposures were for a full 96 hours, with renewal of exposure media 48 hours into the test. The *Chironomus* and *Hyalella* tests were static exposures, but the exposure was for the full 96 hours, not a dip into $KMnO_4$ solutions for one hour followed by transfer into clean water. Hobbs et al. (2006) also measured the residual permanganate ion concentration at both test initiation and at the end of the toxicity tests, unlike nearly all other permanganate toxicity tests. This allowed them to evaluate the degradation of permanganate in test solutions during the test. Finally, Hobbs et al. (2006) exposed their species to two types of dilution water: a synthetic laboratory water with low organic carbon content, and an aquaculture pond water with high (34.81 mg/L) organic carbon content. This design feature of their study allowed them to evaluate the reduction in permanganate ion concentration over time in a water that more closely reflected the types of water in hatcheries to which potassium permanganate is added (i.e. a water with a higher level of organic matter which could be oxidized by permanganate relatively to synthetic laboratory dilution water).

The steepness of the dose-response curve for potassium permanganate, as expressed by the difference between the 96 hour LC_{50} values and the 96 hour NOEC observed by Hobbs et al. (2006), as well as the degradation of $KMnO_4$ in the presence and absence of organic matter is summarized in Tables PP-synthetic and PP-pond. These two tables, which combine information from four separate tables in Hobbs et al. (2006), demonstrate both the narrow range between lethal and no effect concentrations of permanganate, and the effects of organic matter on how long permanganate ion remains in solution.

Table PP-synthetic. Response of five species to potassium permanganate in synthetic laboratory water, and the effects of synthetic laboratory water on $KMnO_4$ concentrations throughout the duration of the exposure (Hobbs et al. 2006).

Species	96-h LC_{50} mg/L	NOEC mg/L	LC_{50}:NOEC	LOEC mg/L	% residual $KMnO_4$ at test completion
Daphnia magna	0.053	0.049	1.08	0.071	Not measured
Ceriodaphnia dubia	0.058	0.047	1.23	0.068	86.5 – 107.8
Pimephales promelas	2.13	1.36	1.57	1.68	95.6 – 101.6
Chironomus dilutus	4.43	<3.20	1.38	3.20	103.0 – 104.7
Hyalella azteca	4.74	3.56	1.33	4.31	95.2 – 108.9

Table PP-pond. Response of five species to potassium permanganate in aquaculture pond water, and the effects of pond water on $KMnO_4$ concentrations throughout the duration of the exposure (Hobbs et al. 2006).

Species	96-h LC_{50} mg/L	NOEC mg/L	LC_{50}:NOEC	LOEC mg/L	% residual $KMnO_4$ at test completion
Daphnia magna	1.98	1.75	1.13	2.50	Not measured
Ceriodaphnia dubia	2.39	2.25	1.06	3.22	5.5 – 17.4
Pimephales promelas	11.28	9.45	1.19	13.50	25.5 – 50.6
Chironomus dilutus	13.55	9.45	1.43	13.50	24.3 – 65.0
Hyalella azteca	12.30	7.83	1.57	11.18	23.1 – 65.0

Several observations are immediately apparent from Tables PP-synthetic and PP-pond. The small concentration range between the NOECs and LC_{50}s is obvious, particularly for the two crustacean zooplankton species *Daphnia* and *Ceriodaphnia*. In synthetic laboratory dilution water, the difference between the NOEC and LC_{50} is 0.004 mg/L and 0.011 mg/L for *Daphnia* and *Ceriodaphnia*, respectively. These differences are equal to one standard deviation in the analytical chemistry quantification of $KMnO_4$ in solution in the Hobbs et al. (2006) study, meaning that the LC_{50} and NOEC values are statistically indistinguishable from each other. Further confirmation of this point is provided by the LOEC values for *Daphnia* and *Ceriodaphnia*, which, in both the synthetic laboratory and aquaculture pond waters, the LOECs are higher than the 96-h LC_{50} values. The ratio between the 96-h LC_{50} and NOEC concentrations in Tables PP-synthetic and PP-pond is the calculation of the LC_{LOW} considered to be the acute NOEC as described in the Problem Formulation. The low values of these ratios, all of which are lower than the national default ratio of 2.27 used to convert a LC_{50} to a LC_{LOW} provides evidence that the use of the 2.27 value to convert an acute LC_{50} to a LC_{LOW} is protective of aquatic species.

Tables PP-synthetic and PP-pond also demonstrate the effect of organic matter on the retention of potassium permanganate in solution. For the tests performed in synthetic laboratory dilution water with low organic carbon content, the concentration of potassium permanganate remaining in solution at test termination is close to 100% of the intended concentration at test initiation. However, for tests performed in aquaculture pond water with elevated total organic carbon concentrations, the amount of potassium permanganate remaining in solution at test termination is as low as 5.5% of the intended concentration at test initiation, and at no time exceeded 65% of the original $KMnO_4$ concentration. Hobbs et al. (2006) also observed that the largest percent reduction in potassium permanganate concentrations occurred in solutions with the lowest added amount of $KMnO_4$, while higher nominal concentrations contained a higher percentage of $KMnO_4$ remaining in solution at test termination. This trend is due to potassium permanganate being added in stoichiometric excess relative to the amount of organic matter in the water at the higher exposure concentrations of $KMnO_4$. This observation, if extended to waters receiving discharges from hatcheries that dilute the hatchery added concentration of $KMnO_4$, leads to a conclusion that permanganate discharges from hatcheries would be reduced in concentration in receiving waters due to $KMnO_4$ oxidizing humic acids and other organic compounds in receiving waters.

Of the available toxicity data, some information on a T&E species under evaluation in this BE is for rainbow trout (steelhead), Chinook salmon and coho salmon. We have used the available 96 hour LC_{50} data under static exposure conditions for rainbow trout, coho salmon and Chinook salmon from Taylor and Glenn (2008) to estimate the toxicity of potassium permanganate to the remaining ESA listed salmonid species in Washington. We have used the methodologies described under the problem formulation section of this BE, specifically using ICE models. We have done this even though the rainbow trout, coho salmon and Chinook salmon 96 hour LC_{50} studies were performed under static exposure conditions, not flow through conditions. Flow through conditions are particularly important for maintaining the desired exposure concentrations of chemicals such as potassium permanganate whose concentrations are quickly reduced when organic matter is present in water, the norm under the environmental conditions in surface waters where T&E species are found. Exposing organisms to reactive oxidant chemicals such as $KMnO_4$ under flow through conditions provides a greater likelihood that the exposure concentrations are as intended throughout the study, relative to the chemical degradation and subsequent reduction in exposure concentration that occurs over time during static or static renewal exposure conditions.

Toxicity of Potassium Permanganate

The only toxicity study with fish meeting EPA requirements for use in developing aquatic life criteria available for potassium permanganate is a flow through exposure study with bluegill

(*Lepomis macrochirus*) (EPA and OPP 2013), which found a 96 hour LC_{50} range of 2300 - 3600 µg/L in a series of three separate toxicity tests. A second fish toxicity study under flow through conditions (Darwish et al. 2002) with channel catfish (*Ictalurus punctatus*) exposed the fish to $KMnO_4$ for only 36 hours, not the required 96 hour exposure needed for inclusion in a dataset useable by EPA to derive acute water quality criteria. Darwish et al. (2002) found 438 µg/L $KMnO_4$ to be a no effect concentration after 36 hours, while 1315 µg/L and 2190 µg/L $KMnO_4$ resulted in 9.4% and 49.6% mortality, respectively, to channel catfish after a 36 hour exposure. The 36 hour exposure duration used by Darwish et al. (2002) is substantially longer than the one hour exposure duration for therapeutic use currently recommended by AFS (2011).

All other fish toxicity data for $KMnO_4$ was performed under static, static renewal or pulsed exposures. Of the available data, the most useful in evaluating potential potassium permanganate toxicity to T&E species in receiving waters is a series of 96 hour LC_{50} studies performed under static exposure conditions on two size classes of rainbow trout, coho salmon and Chinook salmon (Taylor and Glenn 2008). The Taylor and Glenn (2008) toxicity tests were performed at the Abernathy Fish Technology Center of the U.S. Fish and Wildlife Service (Longview, WA) using fish stocks native to Washington (rainbow trout, Chinook salmon) or Oregon (coho salmon), and are part of the same study whose results were used to evaluate toxicity of hydrogen peroxide to T&E salmonid species in this BE.

Taylor and Glenn (2008) exposed two different size classes of fish to potassium permanganate. Their 'small' group of fish had a target body weight of 2 grams, while their 'large' group of fish had a target body weight of 10 grams. Fish were exposed to a potassium permanganate bath of various concentrations for one hour, then placed in clean water for an additional 120 hours to identify any residual mortality response from exposure to the $KMnO_4$ bath. Concentrations of $KMnO_4$ used in the one hour bath were 3, 5, 10, 20, 30, 40, and 50 mg/L. The 96 hour LC_{50} values for rainbow trout, coho salmon and Chinook salmon from Taylor and Glenn (2008) were calculated from a logistic response function. The equation used was that given below.

$$Y_i = \frac{e^{(\beta_0 + \beta_1 x_j)}}{1 + e^{(\beta_0 + \beta_1 x_j)}}$$

Where: Y_i = mortality probability (= 0.50)

β_0 = logistic regression intercept

β_1 = logistic regression slope

x_j = chemical concentration (mg/L)

Calculated 96 hour LC_{50} values are given in Table PP-??? Taylor and Glenn (2008) did not report confidence intervals around their LC_{50} values.

Table PP-??? Empirical 96 hour potassium permanganate LC_{50} values for three salmonid species as reported by Taylor and Glenn (2008).

Species	Size Class	96-hour LC_{50} (mg/L)

Rainbow trout	2 gram body weight	23
Rainbow trout	10 gram body weight	34
Chinook salmon	2 gram body weight	33
Chinook salmon	10 gram body weight	27
Coho salmon	2 gram body weight	43
Coho salmon	10 gram body weight	10

No empirical chronic toxicity data with potassium permanganate are available for rainbow trout, Chinook salmon or coho salmon. Therefore, the procedures given in the Problem Formulation are used to convert the empirical 96 hour LC_{50} values in Table PP-??? to chronic NOEC concentrations. This calculation involves dividing the lower of the two available LC_{50} values for each of the salmonid species in Table PP-??? first by a factor of 2.27 to convert the LC_{50} to an LC_{LOW}, which is considered an acute NOEC. The acute NOEC is then divided by the default national acute-chronic ratio of 8.3 to calculate the chronic NOEC concentrations for rainbow trout, Chinook salmon and coho salmon. The factor of 2.27 is used in this instance to account for the toxicity testing methodology employed by Taylor and Glenn (2008), who exposed their fish for one hour to $KMnO_4$, then placed the fish in clean water for the remainder of the 96 hour study. Most toxicity tests expose organisms to a chemical for the full 96 hours, not one out of 96 hours, thus the need for an additional factor to ensure a conservative, protective estimate of the chronic NOEC. These calculated chronic NOEC values are presented in Table PP-2.

Output of all ICE models run with potassium permanganate for the three remaining T&E species (bull trout, chum salmon and sockeye salmon), genera or family with available data in ICE is shown in Table PP-1 (this is another very wide spreadsheet, in the standalone file "Table PP-1 ICE models for bull trout chum sockeye salmon.xlsx). Using the ICE model selection guidelines set forth in the problem formulation, models used to estimate chronic NOEC's for salmonid species are highlighted in green and bolded in Table PP-1

A genus level ICE model using the empirical coho salmon LC_{50} data (10 mg/L $KMnO_4$, equivalent to 10,000 µg/L, Table PP-???) was used as the starting point to derive chronic NOEC values for bull trout, chum salmon and sockeye salmon. The genus level ICE model using empirical Chinook salmon toxicity data as input could not be used to estimate toxicity to bull trout because the empirical toxicity data was outside of the useable range of the ICE regression between Chinook salmon and bull trout. The genus level ICE model between coho salmon and bull trout, chum and sockeye salmon was selected from the remaining ICE models because of the large number of data pairs in the regression, taxonomic closeness to the modeled species relative to family level ICE models, and high r^2 and cross-validation scores.

The remaining ICE models, with poorer predictive ability and which were not selected as the source of chronic NOEC's are shown in red in Table PP-1. As described in the problem formulation, the lower 95% confidence interval of the predicted chronic NOEC, if available, is used as the chronic NOEC in this BE. All ICE models used for potassium permanganate generated lower 95% confidence intervals of the chronic NOEC, and are shown in this section.

No information is available in ICE for eulachon or any of the T&E rockfish species, genera or families in Washington (bocaccio, canary rockfish, yelloweye rockfish). Therefore, potassium permanganate effects on eulachon and the rockfish species cannot be quantitatively evaluated, and must be considered as a toxicological uncertainty in this BE. However, as the Keta Creek Fish Hatchery discharges into freshwater (Crisp Creek, a tributary of the Green River), not estuarine or marine water, it is unlikely that potassium permanganate discharges from Keta Creek hatchery would impact saltwater species such as eulachon or rockfish.

The final selected chronic NOEC values for bull trout, Chinook salmon, chum salmon, coho salmon, sockeye salmon and steelhead that were compared to the expected environmental concentration of potassium permanganate in receiving water environments are summarized in Table PP-2.

Table PP-2. Chronic no effect concentrations (NOEC) for T&E salmonid species exposed to potassium permanganate.

Species	Chronic NOEC (mg/L)	Source of chronic NOEC
Bull trout	0.440	ICE model – genus level
Chinook salmon	1.43	Empirical acute data (Taylor and Glenn 2008)
Chum salmon	0.798	ICE model – genus level
Coho salmon	0.531	Empirical acute data (Taylor and Glenn 2008)
Sockeye salmon	0.798	ICE model – genus level
Steelhead	1.22	Empirical acute data (Taylor and Glenn 2008)

Risk Characterization: Potassium Permanganate

Risks to T&E Fish Species from Potassium Permanganate

Risks to T&E fish species for which toxic concentrations of potassium permanganate can be identified from the literature are calculated using a standard ecological risk assessment hazard quotient approach. In the hazard quotient approach, the estimated environmental concentration is divided by the chronic NOEC for each T&E species to calculate a hazard quotient. Hazard quotients less than 1.0 are indicative of acceptable levels of ecological risk. In the context of this BE, an acceptable ecological risk is represented as an EEC which, if not exceeded, results in no discernable effect on the survival, reproduction and growth of a T&E species. Note that acceptable chronic NOEC values vary between species. Hazard quotients greater than or equal to 1.0 are indicative of a potential for unacceptable ecological risks to T&E species.

Hazard quotients for the six T&E salmonid species for which toxicity data is available or could be estimated are presented in Table PP-???. Hazard quotients were calculated using the EEC generated from the lowest and highest daily discharge from the Keta Creek hatchery, which results in the largest EEC range to which T&E species could be exposed.

Table PP-??? Hazard quotients (HQ) for T&E species exposed to the range of expected environmental concentrations (EEC) of potassium permanganate discharged by hatcheries.

Species	EEC range (μg/L)	Chronic NOEC (μg/L)	Hazard quotient range
Bull trout	5.7 – 18.2	440	0.013 – 0.041
Chinook salmon	5.7 – 18.2	1430	0.0040 – 0.013
Chum salmon	5.7 – 18.2	611	0.0093 – 0.030
Coho salmon	5.7 – 18.2	531	0.011 – 0.034
Sockeye salmon	5.7 – 18.2	611	0.0093 – 0.030
Steelhead	5.7 – 18.2	1220	0.0047 – 0.015

All hazard quotients in Table PP-??? are substantially lower than 1.0, indicative of acceptable levels of ecological risk to the species under all Keta Creek hatchery discharge scenarios. Note that the EEC values do not take into account the rapid degradation of environmental concentrations of potassium permanganate when it comes into contact with organic matter in surface waters. This is discussed more fully in the uncertainty analysis portion of risk characterization, as it is likely the major uncertainty in this BE which overestimates potential ecological risks to T&E species.

Risks to Potential Freshwater Prey of T&E Species from Potassium Permanganate

Although not of a data quality useful for deriving EPA water quality criteria, a fairly substantial number of species have some potassium permanganate toxicity data available for them (Appendix ???, Table ???). The only toxicity studies with potassium permanganate that may be of a suitable quality for use in EPA water quality criteria derivation, in addition to the bluegill study discussed earlier ((EPA and OPP 2013) are several flow through exposure studies with molluscs. Included among the mollusc studies are several chronic duration (up to 56 days of exposure) survival studies (Klerks and Fraleigh 1991) with zebra mussel (*Dreissena polymorpha*).

Klerks and Fraleigh (1991) determined LT_{50} values (LT_{50} is the length of exposure time needed to kill 50% of test organisms) for zebra mussel to be 10.7, 49.8 and 56 days at $KMnO_4$ exposure concentrations of 1250, 530 and 240 µg/L, respectively. A second series of flow through exposures of zebra mussels to $KMnO_4$ by Klerks et al. (1993) reported that a 14 day exposure to 275 µg/L $KMnO_4$ resulted in 17% mortality.

There are also two flow through studies evaluating the effects of potassium permanganate on survival of Asiatic clam (*Corbicula manilensis*). Chandler and Marking (1979) reported a 96 hour LC_{50} for $KMnO_4$ of 112,000 µg/L (95% confidence interval = 101,000 – 125,000 µg/L). Chandler and Marking (1979) also performed a 96-h static LC_{50} test on *Corbicula manilensis* and observed similar results to their flow through results (96 hour LC_{50} of 118,000 µg/L with 95% confidence limits of 103,000 to 136,000 µg/L. They speculated that the ability of the clams to close their valves during the permanganate exposure may be responsible for both the elevated LC_{50}s and the similarity in the static and flow through LC_{50} concentrations. Cameron et al. (1989) observed that a concentration of 1080 µg/L was a 7.9 day LT_{50} for *Corbicula manilensis* under flow through conditions.

The results of the Hobbs et al. (2006) study of potassium permanganate on *Daphnia magn*a, *Ceriodaphnia dubia*, *Chironomus dilutus* and *Hyalella azteca* have been discussed at length in the introduction to the Measure of Effects section, and will not be repeated here, with the exception of how chronic NOEC concentrations were calculated. Unlike all other available crustacean potassium permanganate toxicity studies, the empirical NOEC is reported for the species studied by Hobbs et al. (2006). Therefore, we concluded that the similarity between the 96-h LC50s and 96-h NOECs from the Hobbs et al. (2006) study provides evidence that dividing the LC50 by the default average ACR (8.0) results in a protective estimate of the chronic NOEC. For *Daphnia* and *Ceriodaphnia*, the two most sensitive crustacean zooplankton species, this calculation resulted in chronic NOEC values of 5.9 µg/L and 5.7 µg/L, respectively.

Most other invertebrate toxicity studies report either LC_{100} values, or LT_{100} values. In the absence of any specific guidance on how to convert such endpoints into chronic NOEC values, we have divided the LC_{100} and LT_{100} values by 2.27, then divided that quotient by 8.3 to obtain chronic NOEC values. The uncertainty in chronic NOEC estimates from this assumption is discussed in the decision rule portion of the Uncertainty Analysis.

Despite the lack of studies of a quality that could be used to develop EPA water quality criteria, we have used the procedures outlined in the Problem Formulation (i.e. divide the acute toxicity value by 2.27 if the exposure duration is shorter than 96 hours for fish or 48 hours for an invertebrate to obtain an LC_{LOW}, or using the empirical acute LC_{50} if the test duration was 96 hours for fish or 48 hours for invertebrates, then dividing the LC_{LOW} or acute toxicity LC_{50} value by a default acute-chronic ratio of 8.3 to obtain a chronic NOEC) to estimate chronic NOEC concentrations for prey of T&E fish species. Chronic NOEC concentrations of potassium permanganate to prey of T&E species is summarized in Table PP-5.

Table PP-5. Toxicity of Potassium Permanganate to Freshwater Prey of T&E Listed Species

Organism Type	Chronic NOEC range (µg/L)
Algae	53 - 1698
Aquatic macrophytes	No data
Aquatic invertebrates	3.6 - 5361
Aquatic insects	534
Crustaceans	5.7 - 531
Zooplankton	5.7 - 422
Molluscs	106 - 5361
Others (e.g. oligochaetes, etc.)	3.6 - 955
Amphibians	No data
Fish	41.9 - 1446

Among the taxonomic groups in Table PP-5, crustacean zooplankton appear to be the most sensitive group, with five of the six available toxicity results having chronic NOEC concentrations of 150 µg/L or lower. The most sensitive freshwater species to potassium permanganate, however, appears to be the oligochaete *Branchiura sowerbyi*, with a four day empirical LC_{50} of 30 µg/L under static exposure conditions (Das and Kaviraj 1994) translating to a chronic NOEC of 3.6 µg/L $KMnO_4$. This oligochaete, along with the zooplankton species *Daphnia magna* and *Ceriodaphnia dubia* are the only prey species whose chronic NOEC is lower than any of the EEC values from the Keta Creek hatchery.

Fish species appear to have an intermediate range of sensitivities to potassium permanganate among the taxa for which empirical toxicity information is available. Algae and molluscs appear to have the widest range of sensitivities to permanganate among taxonomic groups, while the remaining invertebrate species have a narrower range of sensitivities. The most sensitive freshwater fish appears to be the striped bass (*Morone saxatilis*), with a calculated chronic NOEC of 41.9 µg/L. The most tolerant fish species is western mosquitofish (*Gambusia affinis*), with a chronic NOEC of 1446 µg/L.

Only three potential prey species, the crustacean zooplankters *Daphnia magna* and *Ceriodaphnia dubia*, and the oligochaete *Branchiura sowerbyi* has a chronic NOEC lower than any of the EEC values from Keta Creek hatchery. As all other prey species chronic NOECs are higher than the highest EEC for potassium permanganate, we conclude that the weight of evidence for all potential prey species indicates that potassium permanganate is not likely to adversely affect prey species of T&E fish species in Washington.

Uncertainty Analysis of Potassium Permanganate Risk Characterization

All four types of uncertainty (variation, model uncertainty, decision rule uncertainty and true unknowns) described in the problem formulation are present in this potassium permanganate evaluation. By far the largest uncertainty in this evaluation is the complete absence of toxicity data in the literature that would permit a quantitative evaluation of risks to T&E rockfish species from potassium permanganate use at fish hatcheries. This type of uncertainty is a true unknown in this BE. However, as the only Washington hatchery currently using potassium permanganate discharges to a freshwater stream, not to a marine or estuarine system, eulachon and rockfish species are not currently exposed to any potassium permanganate releases from Washington hatcheries.

Variation of expected environmental concentrations in hatchery discharges and receiving waters is also a large source of uncertainty in this analysis. This is because the use pattern of potassium permanganate throughout a year has not been described by the only Washington hatchery that currently reports using $KMnO_4$ in its operations. The absence of the frequency of $KMnO_4$ use or its use patterns means that it is currently uncertain how often potassium permanganate is or is not released from a hatchery. This uncertainty of release to surface waters frequency is a combination of variation in EEC in receiving waters with a true unknown in how often $KMnO_4$ is released from Keta Creek hatchery to surface waters.

Variation also is expressed in the confidence limits surrounding statistically reduced expressions of the empirical toxicity data (e.g. LC_{50}, EC_{50}, etc.). Confidence limits describe random variation around the central tendency response of laboratory organisms exposed to chemicals in toxicity tests. This is an uncertainty regarding the true concentration of $KMnO_4$ that elicits a toxic response in aquatic species.

The environmental degradation rates and short half-life of potassium permanganate in aquatic systems containing organic matter also introduce variation in exposure concentrations and EECs over time. Variation in potassium permanganate concentrations due to its environmental degradation is a unidirectional process, with the environmental concentration constantly declining. Without consideration of the reduction of $KMnO_4$ in surface water to MnO_2, the EEC values used to describe exposure of T&E species to $KMnO_4$ overestimate the concentrations T&E species are actually exposed to in the environment. Not attempting to estimate the effect on potassium permanganate EECs of dilution of hatchery discharges by receiving waters also serves to overestimate the actual EEC to which T&E species are exposed. Although we have estimated EECs without the application of half-lives of $KMnO_4$ presented in this BE, given the already low hazard quotients calculated from our EECs, we have chosen not to modify our EECs by inclusion of a degradation rate term.

EPA normally requires fish toxicity studies used to derive water quality criteria to be performed under flow through conditions. Unfortunately, all but one (EPA and OPP 2013) of the available fish studies of potassium permanganate toxicity were performed under static, static renewal or pulsed exposure conditions. Unless chemical concentrations are frequently monitored, uncertainties exist in the chemical concentrations to which test organisms are exposed in static, static renewal or pulsed exposures. This is particularly true for chemicals having the potential to degrade rapidly, which is the case for potassium permanganate coming into contact with organic matter. This uncertainty can be quantitatively evaluated to an extent by comparing the potassium permanganate 96 hour LC_{50} values for bluegills exposed in flow through (EPA and OPP 2013) and static (Marking and Bills 1975) exposures. The range of the three individual flow through LC_{50} values (2300 – 3600 μg/L) from EPA and OPP (2013) and the single LC_{50} from Marking and Bills (1975) of 2380 μg/L overlap. This overlap in the LC_{50}s obtained under flow through and static exposure conditions provides some level of confidence that static LC_{50}s for $KMnO_4$ may not substantially underestimate the toxicity of potassium permanganate.

Decision rule uncertainty came into play during the evaluation of potassium permanganate risks. This is because nearly all of the toxicity studies were not performed using standardized test protocols. For acute toxicity, standard protocols call for exposing an animal to the test chemical for either 48 hours (invertebrates) or 96 hours (fish). Many permanganate studies exposed organisms to a permanganate bath for a short time period (one hour or less), then transferred the animals into clean water for the duration of the test. While this exposure scenario mimics the use of potassium permanganate at hatcheries, the problem formulation methodology was not designed to evaluate toxicity from this type of non-standard exposure. Therefore, we modified the usual chronic NOEC estimation procedure to account for this type of non-standard exposure scenario. Other permanganate toxicity studies expressed results in terms of the length of time required to kill 100% of test organisms. While an appropriate experimental design for a chemical whose intended use is as a biocide, measurement of a LT_{100} is also a non-standard toxicity test procedure, at least during the derivation of EPA water quality criteria, and thus required a modification to the decision rules on how to convert 48 or 96-h LC_{50} values to chronic NOECs.

Model uncertainty in the ICE models is described by the percent cross-validation success statistic. According to Raimondo et al. (2013), the percent cross-validation success rate for each model is the proportion of data points that are predicted within 5-fold of the actual LC_{50} value. There is a strong relationship between taxonomic distance and cross-validation success rate, with uncertainty generally, although not always increasing with larger taxonomic distance. Maximizing the value of the cross-validation statistic was a primary determinant of which of multiple ICE models were used to estimate toxicity values in this BE for species where no empirical toxicity data exists for a chemical-species pair.

Effect Determinations of Potassium Permanganate on T&E Species

Based on all chronic NOEC concentrations for six T&E salmonid species being substantially higher than the estimated environmental concentrations of potassium permanganate released from hatcheries, EPA has made the following effect determinations for potassium permanganate:

Bull trout: Not likely to adversely affect

Chinook salmon: Not likely to adversely affect

Chum salmon: Not likely to adversely affect

Coho salmon: Not likely to adversely affect

Sockeye salmon: Not likely to adversely affect

Steelhead: Not likely to adversely affect

The above determinations are all based on the estimated environmental concentrations from hatchery releases being substantially lower than the chronic NOECs for the above six species.

Based on the lack of current discharges from any Washington hatchery directly into estuarine or marine waters, the following species are not exposed to potassium permanganate releases from Washington hatcheries. Therefore, a no effect determination from potassium permanganate released by hatcheries is warranted for the following species.

Eulachon: No effect

Bocaccio: No effect

Canary rockfish: No effect

Yelloweye rockfish: No effect

These no effect determinations would need to be revisited if hatcheries which discharge directly into estuarine or marine systems would begin to use potassium permanganate in their operations at some future date.

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